Supplementary Information Controlled synthesis of conjugated random copolymers in a droplet-based microreactor

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Precursor preparation

Preparation of 2-bromo-5-chloromagnesio-3-hexylthiophene / 2-chloromagnesio-5bromo-3-hexylthiophene, ~80:20 mix (**1b**, 0.25M):

0.75 ml (1.5 mmol, 1 equiv.) of 2M isopropylmagnesium chloride solution (Aldrich) was added dropwise from a syringe at room temperature to an oven-baked flask containing 0.5 g (1.5 mmol) of degassed 2,5-dibromo-3-hexylthiophene, **1a**, (Lanzhou Galaxy, >99 % by 1H NMR) in 5 ml of anhydrous THF. The solution was heated to 55 °C for 30 minutes yielding a pale yellow mixture, **1b**, which was transferred to a 10 ml gas-tight syringe (SGE) and isolated from the atmosphere prior to use.

Preparation of 2-bromo-5-chloromagnesio-3-hexylselenophene / 2-chloromagnesio-5-bromo-3-hexylselenophene, ~80:20 mix (**2b**, 0.25M):

2b was prepared in analogous fashion to **1b**, using n-butylmagnesium chloride solution (Aldrich) (2M in THF) and 0.56 g (1.5 mmol) of 2,5-dibromo-3-selenothiophene, **2a** (synthesised according to literature methods^{1,2}).

Configuration of complete droplet reactor

The complete reactor set-up is shown in Fig. S1a. The two monomers, catalyst solution and PFPE were loaded into four separate gas-tight syringes (Hamilton/SGE), and each was mounted onto its own dedicated syringe pump (Harvard Apparatus Pump 11+). PTFE tubing was connected to the various fluidic components using flangeless fittings (Upchurch). Syringe pumps P1 and P2 injected reagents **1b** and **2b** into the Y-shaped mixer M (Upchurch), the outlet of which was connected to one of the two side-inlets of the droplet generator. Syringe pump P3 injected PFPE carrier fluid into the central inlet of the droplet generator, while syringe pump P4 injected the Ni(dppp)Cl₂ catalyst solution into the other side-inlet of the droplet generator. The droplet generator outlet was connected to a length of PTFE tubing, 2 m of which was immersed in a heated oil-bath. The product was collected in vials at position C. A close-up of the mixing and droplet generation stages is shown in Fig. S11b.



Fig Sl1 – (a) A photograph of the full reactor setup and (b) a close-up photograph of the monomer-mixing and droplet-generation stages. A two-way y-shaped mixer (M) is used to merge the two monomer streams **1b** and **2b**, and a three-way droplet generator (DG) is used to form droplets of the pre-mixed monomers and the Ni(dppp)Cl₂ catalyst solution in the PFPE carrier fluid. The polymerization takes place in the heated reaction zone R.

Fabrication of Droplet Generators

The droplet generators were fabricated in-house, using a 4-dimensional CNC mill to machine PTFE round-stock (RS). As shown in Fig SI2a, the droplet generators had 1 mm through-channels and were interfaced with the capillary tubing using flangeless ferrules and nuts (Upchurch). For illustrative purposes, otherwise-identical droplet generators were fabricated in semi-translucent PCTFE (Polyflon). The internal channel structure is clearly visible in Figs. SI2b,c. Connections to external tubing were made with a ¼"-28 UNF screw thread tapped into the structure (see Fig SI2c).



Fig SI2 – Schematic of droplet generator (a). Translucent PCTFE droplet generator viewed in perspective (b) and from above with fluidic connections in place (c). (Note a central portion of the PCTFE round-stock has been milled out to improve the visibility of the channels).

Droplet generation

The process of droplet generation is illustrated in Fig. SI3a-c. PFPE carrier fluid was pumped through the central channel (left-to-right), while orange-coloured Sudan dye (Aldrich) in THF was introduced through the two side inlets, creating a stream of droplets in the exit channel. The droplet dimensions are controlled by the diameter of the tubing and the relative injection rates of the carrier and reagent-phases, higher carrier flow-rates giving rise to a larger number of smaller droplets.



Fig SI3 – Close up of droplet generation process in a translucent PCTFE droplet generator. PFPE carrier fluid is injected into the central channel, while orange dye is injected into the two side channels. The orange dye accumulates at the point of confluence (a) and steadily increases in volume (b) until it buds off as a discrete droplet (c).

Reactor Fabrication

The heated section of the PTFE tubing was held in a shallow bath (Figure SI4) that was 3D printed from polylactic acid (PLA). Holes within six symmetrically arranged spokes, extending radially from the circumference towards the centre of the bath, allowed 2 m of tubing to be neatly coiled in a flat spiral arrangement without twisting or kinking. The bath was filled with paraffin oil and placed on a uniform temperature-stabilised hotplate with a stirrer bar placed in the centre to further homogenise the temperature. The direction of droplet flow was from the centre of the spiral (where the coil is tightest) outwards. On leaving the oil bath the droplets (and carrier fluid) were immediately collected in a methanol-filled vial to induce precipitation.



Fig. SI4 – photograph of 3D-printed oil-bath used for securing and heating the PTFE tubing.

Flow Conditions

The total flow rate of the total monomer feed was maintained at 54 μ L/min and the ratio of infusion rates for **1b** and **2b** was varied to achieve a series of copolymers according to Table SI1.

Table SI1 Thiophene and selenophene infusion rates used to prepare the series of P3HT-co-P3HS copolymers.

Sample	% selenophene	F _{3HS} (mL/min)	F _{знт} (mL/min)
P3HT	0	-	54.00
25 % Se	25	13.50	40.50
33 % Se	33	18.00	36.00
50 % Se	50	27.00	27.00
67 % Se	67	36.00	18.00
75 % Se	75	40.50	13.50
83 % Se	83	45.00	9.00
P3HS	100	54.00	-

Full 1H NMR Characterisation



P3HT: ¹H NMR (400 MHz, CDCl₃): δ 7.00 (s, 1H, A), 6.95 (s, 1H, A), 2.84 (m, 2H, B), 1.73 (m, 2H, C), 1.69-1.27 (m, 6H, D-F), 0.95 (t, *J* = 6.9 Hz, 3H, G)

25 % Se: ¹H NMR (400 MHz, CDCl₃): δ 7.21 (s, 1H, A), 7.15 (s, 1H, A), 7.00 (s, 1H, A), 6.94 (s, 1H, A), 2.80 (m, 2H, B), 1.71 (m, 2H, C), 1.67-1.24 (m, 6H, D-F), 0.94 (t, *J* = 6.6 Hz, 3H, G)

33 % **Se:** ¹H NMR (400 MHz, CDCl₃): δ 7.21 (s, 1H, A), 7.14 (s, 1H, A), 7.00 (s, 1H, A), 6.94 (s, 1H, A), 2.79 (m, 2H, B), 1.71 (m, 2H, C), 1.67-1.24 (m, 6H, D-F), 0.94 (t, *J* = 6.8 Hz, 3H, G)

50 % Se: ¹H NMR (400 MHz, CDCl₃): δ 7.22 (s, 1H, A), 7.15 (s, 1H, A), 7.01 (s, 1H, A), 6.95 (s, 1H, A), 2.79 (m, 2H, B), 1.71 (m, 2H, C), 1.67-1.24 (m, 6H, D-F), 0.95 (t, *J* = 6.4 Hz, 3H, G)

67 % Se: ¹H NMR (400 MHz, CDCl₃): δ 7.20 (s, 1H, A), 7.14 (s, 1H, A), 6.99 (s, 1H, A), 6.94 (s, 1H, A), 2.77 (m, 2H, B), 1.70 (m, 2H, C), 1.65-1.24 (m, 6H, D-F), 0.93 (t, *J* = 6.8 Hz, 3H, G)

75 % Se: ¹H NMR (400 MHz, CDCl₃): δ 7.21 (s, 1H, A), 7.15 (s, 1H, A), 7.00 (s, 1H, A), 6.94 (s, 1H, A), 2.80 (m, 2H, B), 1.69 (m, 2H, C), 1.65-1.25 (m, 6H, D-F), 0.94 (t, *J* = 6.6 Hz, 3H, G)

83 % Se: ¹H NMR (400 MHz, CDCl₃): δ 7.20 (s, 1H, A), 7.14 (s, 1H, A), 7.00 (s, 1H, A), 6.94 (s, 1H, A), 2.76 (m, 2H, B), 1.70 (m, 2H, C), 1.51-1.24 (m, 6H, D-F), 0.93 (t, *J* = 6.8 Hz, 3H, G)

100 % Se: ¹H NMR (400 MHz, CDCl₃): δ 7.14 (s, 1H, A), 2.75 (m, 2H, B), 1.71 (m, 2H, C), 1.65-1.24 (m, 6H, D-F), 0.93 (t, *J* = 6.8 Hz, 3H, G).

Characterisation Methods

Nuclear Magnetic Resonance was performed on a Bruker AV-400 NMR machine (400 MHz) in CDCl₃. 1H NMR was recorded in the range 0-10 ppm against a TMS reference. Regioregularity was determined from the methylene proton integrals at 2.50-2.60 ppm (ir) and 2.75-2.84 ppm (r) using the formula: $r/(ir+r)\times100$ %, taking into account movement of the peak as the signal shifted with %Se.

UV-Visible absorption spectra were measured using a Fluoromax-2 fluorimeter fitted with a transmission detector.

Refractive Index Size-Exclusion Chromatography (RI-SEC) was performed using an Agilent 1200 Series GPC-SEC Analysis System fitted with two PLgel mixed-B columns in series running a chlorobenzene eluent and calibrated to polystyrene standards. All samples were washed with excess methanol to remove monomer, dried, redissolved in chlorobenzene and filtered with a 0.2 μ m PTFE filter to remove particulate matter. Polymer eluted between 14 and 18 minutes.



Fig. SI5 – RI-SEC chromatogram for copolymers

Fig. SI5 shows RI-SEC chromatograms for the series of P3HT-co-P3HS copolymers. In all cases the dominant product was polymer with Mn values in the range 36 - 44 kDa; also present at <1.5 wt% was a ~5 kDa oligomeric side product that if required could be removed by a further Soxhlet extraction in hexane. Number-average (Mn) and weight-average (Mw) molecular weights for the polymer component, together with the corresponding polydispsersity indices (PDI = Mw/Mn) are listed in Table SI1.

Sample	M _n (kg/mol)	M _w (kg/mol)	PDI
P3HT	36	48	1.3
25 % Se	42	55	1.3
33 % Se	43	58	1.3
50 % Se	36	50	1.4
67 % Se	41	58	1.4
75 % Se	43	62	1.4
83 % Se	39	59	1.5
P3HS	44	62	1.4

Table SI2 Molecular weight data of each (co-)polymer sample.

References

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